

A Study of the Active Modifications of Hydrogen

By Hugh M. Smallwood

A dissertation submitted to the Board of University Studies
of the Johns Hopkins University in conformity with the
requirements for the degree of Doctor of philosophy

June 1927

Baltimore

1929



Digitized by the Internet Archive
in 2026

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

AN ATTEMPT TO PREPARE TRIATOMIC HYDROGEN¹

BY HUGH M. SMALLWOOD² AND H. C. UREY

RECEIVED JUNE 9, 1927

PUBLISHED MARCH 7, 1928

Introduction

The preparation and properties of an active modification of hydrogen, supposed to be triatomic, have been described by a number of investigators.³ According to their papers, whenever hydrogen is ionized or dissociated a small amount of active product is formed. The activating agents that have been used with success include α -particles, the Siemens ozonizer, the vacuum discharge and the corona discharge. It has also been stated that if oxygen is burned in an atmosphere of hydrogen, or if hydrogen-oxygen mixtures containing deficiency of oxygen are detonated, part of the hydrogen remaining after the combustion is activated. It has furthermore been reported that hydrogen is activated by passage over

¹ Extract from Dissertation submitted by Hugh M. Smallwood in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Du Pont Fellow in Chemistry.

³ (a) Duane and Wendt, *Phys. Rev.*, [2] 10, 116 (1927); (b) Wendt and Landauer, *THIS JOURNAL*, 42, 930 (1920); (c) 44, 510 (1922); (d) Newman, *Phil. Mag.*, 43, 455 (1922); (e) Venkataramaiah, *Nature*, 106, 46 (1920); (f) 112, 57 (1923); (g) *Chem. News*, 124, 323 (1922); (h) *THIS JOURNAL*, 45, 261 (1923); (i) Venkataramaiah and Swamy, *Proc. Sci. Ass. Mah. Coll. Viz.*, p. 23, Dec., 1922; (j) Grubb, *Nature*, 111, 600, 671 (1922); (k) Paneth, *Z. Elektrochem.*, 30, 504 (1924); (l) Anderegg, *THIS JOURNAL*, 47, 2429, (1925).

heated metals such as platinum and palladium. Of these various methods of preparation the passage of hydrogen over heated metals or through the ozonizer is said to be the most readily performed.

This modification of hydrogen has been reported to have the property of reducing sulfur, arsenic, phosphorus, nitrogen, etc., at room temperature to form the corresponding hydrides, and it is this characteristic that has been used to test for the material. It is not completely destroyed upon passage through glass wool, as is monatomic hydrogen, and it is described as having a period of half-life of the order of several minutes. It retains its activity upon condensation at liquid air temperatures and subsequent evaporation. Wendt and Landauer^{3b,c} state that it is catalytically decomposed by platinum, nickel, copper, lead, antimony and cadmium, but that it is not affected by silver, molybdenum, mercury, tin, bismuth, zinc or aluminum. They further observed that its preparation in a closed system is accompanied by a decrease in pressure. It is this observation that has led to the assumption of a triatomic molecule.

Recent workers, however, have been unable to duplicate these results. Bach,⁴ Scanavy-Grigoriowa⁵ and Paneth, Klever and Peters⁶ were unable to obtain evidence of activation upon passing hydrogen over heated metals. The latter authors also report unsuccessful attempts with the ozonizer, bombardment with α -particles and detonation of hydrogen-oxygen mixtures. Curtius,⁷ moreover, was unable to obtain activation with the ozonizer. On the other hand Elliott,⁸ working with a similar apparatus, reports a large number of positive results including quantitative studies of the effects of the conditions of the various experiments upon the extent of activation.

There are therefore many contradictions in the past work on active hydrogen. The present paper describes a series of experiments attempting the preparation of this active hydrogen. The methods of the former workers have been repeated and, in some cases, extended. Throughout the work the results have been negative.

Experimental

1. **Corona Discharge and Ozonizer.**—The apparatus used in these experiments and those to be described was built of Pyrex glass throughout. The corona tube was similar to that employed by Wendt and Landauer in the previous work on this method. It consisted of a Liebig condenser about 1 m. long. The high tension electrode was a bare aluminum wire, 0.6 mm. in diameter, strung along the axis of the central tube of the condenser by means of tungsten hooks, the latter being sealed through the glass at each end of the central tube. A salt solution circulated through the cooling jacket

⁴ Bach, *Ber.*, **58B**, 1388 (1925).

⁵ Scanavy-Grigoriowa, *Z. anorg. allgem. Chem.*, **159**, 55 (1926).

⁶ Paneth, Klever and Peters, *Z. Elektrochem.*, **33**, 102 (1927).

⁷ Curtius, *Diss.*, Heidelberg, 1926.

⁸ Elliott, *Trans. Faraday Soc.*, **23**, 60 (1927).

served as the ground electrode. The central tube, through which the hydrogen passed, was 1.2 cm. in diameter. The tube was operated at a potential of 11–12 kv. with 60 cycle alternating current. This gave a fairly uniform discharge from the central wire.

The method used to determine the extent of activation was first developed by Wendt and Landauer.^{3b,c} It is carried out as follows. After leaving the discharge the hydrogen is passed over glass wool (to remove atomic hydrogen) and is then mixed with nitrogen, the resulting mixture being scrubbed with 100 cc. of water. The presence of an active form of hydrogen results in the formation of ammonia, which is absorbed in the scrubbing water and determined by the usual Nessler test. The delicacy of this test was shown in the blank runs. These showed the absence of ammonia in the hydrogen and nitrogen used, but upon passing the hydrogen through the discharge without subsequent mixing with nitrogen, ammonia was found to be present to the extent of 0.0001% of the hydrogen passed. Presumably this was caused by the impurity of the original hydrogen. Both the hydrogen and the nitrogen were taken from cylinders, the nitrogen being bubbled through alkaline potassium pyrogallate and concentrated sulfuric acid.

Two thirty minute runs with this apparatus in which the pressure was maintained at one atmosphere and the temperature at room temperature, the rates of flow being 1400 and 180 cc. (0° and 760 mm.) of hydrogen per minute, respectively, failed to show an appreciable activation of the hydrogen in that the test for ammonia was no larger than that appearing in the blank run. The linear velocities of the gas flowing varied from 160 cm. to 1200 cm. per minute and the time spent in the ozonizer from 0.6 to 0.08 minute. This appears to be a sufficiently high velocity to insure removal from the activating zone and a sufficient time in the ozonizer to secure activation. Wendt and Landauer report only the volumes of hydrogen flowing per minute and not the dimensions of the apparatus, but from their description of their apparatus we believe that we have used both a wider range of linear velocities and times of activation than did these authors.

It was thought that this failure might be due to aluminum sputtered off the central electrode onto the glass walls. To remove this difficulty a Pyrex tube 4 mm. in diameter was inserted in place of the central electrode, being supported by a ring seal at each end. This tube was filled with salt solution and connected to the high tension terminal of a large spark coil. A uniform brush discharge throughout the tube was obtained with this set-up. Before commencing the actual runs the inside of the discharge tube was washed out with dilute hydrochloric acid and distilled water. Several half hour runs at atmospheric pressure and rates of flow of 400 to 800 cc. of hydrogen per minute gave no indication of the presence of an active form of hydrogen.

2. Combustion of Oxygen in Hydrogen.—The apparatus used was essentially the same as that employed by Venkataramaiah in the original work on this method. A large bulb was filled with hydrogen and the rate of flow of hydrogen through the bulb adjusted to a convenient value. Oxygen was then admitted through a platinum jet (8 mm. in diameter) and ignited by means of sparking points sealed through the wall of the bulb near the jet. The oxygen stream was regulated to give a flame about 3 cm. long. The products of combustion were passed through glass wool, over flowers of sulfur and finally directed against a piece of filter paper dipping into lead acetate solution. No formation of hydrogen sulfide could be detected with this apparatus.

3. Passage of Hydrogen over Hot Wires.—Hydrogen was passed over an electrically heated coil of nickel wire hung loosely from a horizontal porcelain tube. The temperature of the wire was varied from a dull red to the melting point of nickel. The rate of flow of hydrogen was varied through wide limits and in some experiments the gas was saturated with water by bubbling through water prior to entering the apparatus.

The hydrogen leaving the apparatus was led over flowers of sulfur and tested with

lead acetate. No indications of the presence of an active modification of hydrogen were obtained although each new piece of nickel wire produced a very minute amount of hydrogen sulfide. In the light of the work of Bach and others (*loc. cit.*) these faint tests were interpreted as being due to some form of sulfur present in the original wire but which was soon exhausted.

Further experiments with platinum wires and the tungsten filament from a Mazda lamp gave no tests for hydrogen sulfide, although in some cases the wire was hot enough and the flow of hydrogen sufficiently great to melt the sulfur and even distil it into the lead acetate solution.

4. Vacuum Discharge.—The major part of the time spent on this research was devoted to an effort to determine whether or not an active modification of hydrogen capable of passing through a plug of glass wool is present in the gases drawn from a vacuum discharge.

Throughout this part of the work electrolytic hydrogen was used, the electrolyte being a 30% solution of potassium hydroxide. The hydrogen was passed through asbestos to remove as much as possible of the alkaline spray, and then passed over heated platinized asbestos to remove any trace of oxygen. In some experiments the hydrogen was dried with liquid air.

The first apparatus set up was, as nearly as possible, an exact replica of that used by Wendt and Landauer. This consisted of a discharge tube 10 cm. long from which the hydrogen was led over glass wool, then over flowers of sulfur and finally over a strip of filter paper dipping in lead acetate solution. No hydrogen sulfide was formed in this apparatus upon running it for as long as half an hour, although Wendt and Landauer report large tests at the end of three minutes. The pressure in the discharge was varied from 2 to 7 cm. of mercury and the rate of flow of hydrogen was varied through a wide range.

This method of detecting a small amount of hydrogen sulfide does not seem particularly delicate. To remedy this defect and to permit working at lower pressures another procedure was developed. The lead acetate bubbler was replaced with a trap filled with silica gel, which was activated by heating at 300–350° for one hour in a current of hydrogen at a pressure of 1–2 mm. The apparatus was then filled with hydrogen at atmospheric pressure and the gel heated for another fifteen minutes in a slow current of hydrogen which was led out of the apparatus and bubbled through a solution of lead acetate acidified with acetic acid. This was done to show that all of the sulfur had been removed from the gel. If this blank was satisfactory a run was made during which the gel was cooled with liquid air. At the conclusion of the run the apparatus was again filled with hydrogen and the heated gel swept out into the lead acetate solution as before. Although much more laborious than the methods used by previous workers, this procedure enabled the detection of exceedingly minute amounts of hydrogen sulfide.

On using this more delicate test it was found to be extremely difficult to obtain good blank tests. Commercial flowers of sulfur were found to contain fairly large amounts of volatile sulfides. To remedy this a very pure form of sulfur was prepared by acidifying a solution of sodium thiosulfate with hydrochloric acid and filtering off and distilling the precipitated sulfur. It was next found that in the course of a thirty-minute run enough sulfur could distil over into the gel to give fairly large amounts of lead sulfide, the elementary sulfur, of course, being reduced upon passing through the heated gel in the presence of hydrogen. This effect was eliminated by adjusting the Dewar flask holding the liquid air, in which the gel was immersed, in such a manner that the liquid air level stood 5–10 cm. above the top of the gel. The sulfur condensed to an opalescent film immediately upon reaching the cold tube. Upon removing the liquid air the hydrogen sulfide evaporated and could be swept out of the gel by heating

without disturbing the sulfur condensed some distance away. Employing these precautions it was found possible to obtain perfect blank tests both upon running the discharge with no sulfur in the apparatus and upon passing the hydrogen over the sulfur in the absence of the discharge.

In the course of an actual experiment the hydrogen passed out of the discharge, through a plug of glass wool 10 cm. long and finally over the sulfur. At this point any of the active form present would react to form hydrogen sulfide, which would be adsorbed on the gel and would, at the end of the experiment, be made evident by the precipitation of lead sulfide. Such experiments frequently resulted in the formation of a small amount of precipitate but the tests so obtained were so minute and erratic that they could not be definitely ascribed to the presence of an active modification of hydrogen.

The conditions under which the various experiments were carried out were as follows. The pressure was varied in different runs from 1 to 80 mm. At the lower pressures rates of flow of 20–30 cc. per minute were used and at the higher pressures the rate was maintained at 200 cc. per minute, both volumes being measured under standard conditions. Throughout the low pressure work Wood⁹ discharge tubes about 1 m. long were used. These were run with wet hydrogen, giving the red discharge due to atomic hydrogen, and with dry hydrogen, in which case the secondary spectrum was most prominent. The hydrogen to be tested was tapped off either in the middle of the tube or near one of the electrodes, since Smyth and Brasefield¹⁰ have found that at that point in the discharge there are large amounts of H_3^+ . The sulfur was inserted 15–30 cm. away from the discharge, connection being made with 7mm. glass tubing. In some of the experiments the discharge tube was cooled with tap water, with salt-ice mixture or with carbon dioxide snow and ether.

The experiments at higher pressures were carried out in smaller discharge tubes of the general type used by Wendt and Landauer. These were water cooled throughout. In some cases a condensed discharge was used, producing the atomic spectrum at a pressure of several centimeters.

During the whole series of experiments sporadic tests were obtained but these were so small that it was necessary to run for thirty minutes or more in order to produce a visible amount of lead sulfide. The size of the tests seemed to have no connection at all with the experimental conditions under which they were obtained. Efforts to show that the substance producing them was unstable enough to decay when led through a by-pass 4 m. long and 2 cm. in diameter before reaching the sulfur were not conclusive because of the strong fatigue effect observed in all the tubes. Attempts to rejuvenate a spent tube by washing with dilute hydrochloric acid, sodium hydroxide and distilled water were only partially successful. The great difficulty encountered in the whole work was that it was not possible to make a series of consistent runs in order to determine, for example, whether or not cooling the discharge had any effect on the size of the precipitate. No tube could be found that, when operated under identical experimental conditions, would give the same amount of lead sulfide three times in succession.

Wendt and Landauer have sought to obtain evidence for their assumption of a triatomic molecule by showing that the activation of hydrogen in a closed system is attended with a decrease in pressure. This experiment has been repeated and part of the original results confirmed. The apparatus used consists of a U-shaped discharge tube equipped with platinum electrodes and attached to a small closed arm manometer. If a discharge is passed at a hydrogen pressure of 9 cm. of mercury and at liquid air temperatures, there is a considerable pressure drop provided the electrodes are immersed

⁹ Wood, *Proc. Roy. Soc. (London)*, **97**, 455 (1920).

¹⁰ Smyth and Brasefield, *Proc. Nat. Acad. Sci.*, **12**, 443 (1926).

in the liquid air. If, however, the electrodes are not immersed in liquid air there is no effect. Wendt and Landauer report that the discharge has a yellow or greenish yellow color. In the repetition the discharge was the usual pale blue color throughout.

Discussion

The experiments just described indicate that, under the experimental conditions detailed, there is no appreciable activation of hydrogen. The failure of duplication of the results of the original workers may be accounted for in a number of ways. In the first place none of the papers announcing positive results report adequate blank experiments. All of the investigators were careful to ensure the absence of the particular hydride which was later to form the test from the hydrogen used in the work, but none report experiments designed to show that there was no source of sulfur or nitrogen, as the case might be, sufficiently near to the activating agent to cause the tests. Thus a little elementary sulfur blown back into a discharge can account for many of the results ascribed to H_3 . On the other hand, the experiments described by Duane and Wendt and by Wendt and Landauer were so numerous and of such varied nature that it is difficult to account for them by assuming contamination of the apparatus. Although Elliott's results are detailed and self-consistent they are open to criticism on the ground that he did not sufficiently guard against the possibility of sulfur dust being blown back into the discharge. If his results were due to an active hydrogen, they fail to check those of previous workers in a number of instances. Thus he finds a much shorter period of half life than that reported by Duane and Wendt. This fact suggests a correlation between his work and that of Anderson¹¹ and of Mitchell and Marshall,¹² who found that the temperature at which copper oxide begins to react with hydrogen is decreased if platinum is placed in the hydrogen stream a short distance in front of the copper oxide. They showed that the effect was due to an unstable modification of hydrogen with an extremely short life. It is possible that some of these positive results may have been due to hydrogen molecules in metastable vibrational and rotational state. The question of blank tests, however, certainly deserves more attention than it has received. All of the papers, excepting the two last cited, in which the necessary controls are reported, record uniformly negative results.

An unknown catalytic effect might account for the uncertainty of the results. This could hardly be an anticatalytic effect since cylinder hydrogen has been used successfully. On the other hand, the hydrogen used in the greater part of the previous work could only have contained minute traces of water vapor, nitrogen or argon. The hydrogen used in the present work must have contained all of these gases as impurities

¹¹ Anderson, *J. Chem. Soc.*, **121**, 1153 (1922).

¹² Mitchell and Marshall, *ibid.*, **123**, 2448 (1923).

at one time or another. It seems unlikely that it is a question of the catalytic effect of the walls of the apparatus since, if this were the case, it should have been observed by the first workers in the field.

The pressure drop experiments fail to add any evidence since hydrogen is readily taken up by metallic electrodes and may be driven into the glass walls to an appreciable extent. In this connection it is interesting to note that in 1908 Fischer and Iliovici¹³ subjected hydrogen at atmospheric pressure and liquid air temperatures to the silent discharge in a tube with *external* electrodes. They found a decrease in pressure of 0.5 mm. but, since this was less than their experimental error, they concluded that there is no new molecular species formed under these conditions. Wendt and Landauer's work would lead one to expect a large pressure drop in such an experiment. Furthermore, the pressure drop observed by them and duplicated by us was so large that, had it been due to the formation of H_3 , it is extremely unlikely that the other experiments with the vacuum discharge would have been negative.

The only conclusion that can be drawn, therefore, is that the existence of triatomic hydrogen has not yet been established. Assuming that there is such a substance, however, it is more difficult to prepare than has been formerly supposed.

Summary

1. Unsuccessful attempts to prepare H_3 by means of the corona discharge, ozonizer, combustion of oxygen in hydrogen, passage of hydrogen over hot metals and the vacuum discharge are described.
2. The previous work on this subject is discussed with the conclusion that the existence of H_3 is not as certain as has been supposed.

BALTIMORE, MARYLAND

¹³ Fischer and Iliovici, *Ber.*, **41**, 4452 (1908).

[Reprint from the Journal of the American Chemical Society, **51**, 1985 (1929).]

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE RATE OF RECOMBINATION OF ATOMIC HYDROGEN

BY HUGH M. SMALLWOOD

RECEIVED JANUARY 31, 1929

PUBLISHED JULY 5, 1929

It has been pointed out by a number of investigators¹ that certain exothermic reactions of the type $A + B \longrightarrow AB$ cannot result from simple binary collisions of molecules A and B since, in such a collision, there is no means by which the energy corresponding to the heat of the reaction may be removed from the colliding molecules. In order to react the molecules must collide in the immediate neighborhood of some other object such as another molecule or the wall of the containing vessel. In other words, the reaction can only take place as the result of triplet impacts or three-body collisions.

A few limitations must be made to the foregoing statement. Thus, if there is a possibility of radiation occurring during the collision of molecules A and B, combination may result from a single collision since the energy of combination may be radiated from the system as light. Further, if molecules A and B are relatively complex, the energy of combination may be taken up by their internal degrees of freedom.

¹ Boltzmann, "Gastheorie. II," Leipzig, 1912; Herzfeld, *Z. Physik*, **8**, 132 (1922); Born and Franck, *Ann. Physik*, **76**, 225 (1925); *Z. Physik*, **31**, 411 (1925); J. H. Jeans, "The Dynamical Theory of Gases," 4th ed., Cambridge University Press, p. 195.

There are therefore only a few reactions which may be expected to proceed according to the predicted three-body mechanism. One of these, however, is the recombination of atomic hydrogen, represented stoichiometrically by the reaction $\text{H} + \text{H} \rightarrow \text{H}_2$. The present paper describes a measurement of the rate of this reaction at various pressures. The results obtained are in agreement with the predicted mechanism.

The method used was to allow dissociated hydrogen drawn from an electric discharge to pass along a straight tube.² The degree of dissociation of the hydrogen at varying distances along this tube was determined by measuring the heat effect produced upon a piece of platinum foil placed in the flowing gas at the desired distance from the discharge. Wood² has shown that metals cause the complete recombination of the atomic hydrogen. Since the heat of this recombination is known and since the rate of flow can be measured, the degree of dissociation is readily calculated.

Experimental

Source of Hydrogen.—Throughout these experiments the hydrogen was taken from a water-cooled electrolytic generator using as electrolyte a 30% solution of potassium hydroxide containing a little barium hydroxide. The hydrogen so obtained contains about 3% of water vapor. Since the presence of this water vapor has been shown to be necessary for the production of the atomic hydrogen, no attempt was made to remove it.

Since the presence of this water vapor has been shown to be necessary for the production of the atomic hydrogen, no attempt was made to remove it.

Apparatus.—Figure 1 shows the essential parts of the apparatus finally adopted. Hydrogen from the generator (not shown) was admitted at A and expanded through the capillary B to a pressure of a few tenths of a millimeter. It was then led to the discharge tube C, which was immersed in a water-bath. While in the discharge tube the hydrogen was almost completely dissociated, so that recombination took place along the vertical tube, ab. The pressure at each end of this tube could be measured on a

McLeod gage by means of the connections shown in the sketch. D is a calorimeter (shown in detail in Fig. 2) which could be slid up or down the tube ab. The calorimeter was made in the shape of a small Dewar flask with a hole in the bottom, the joint between the calorimeter and the central tube ab being made water tight by means of a short piece of gum tubing, E. The calorimeter was flared slightly at the top to permit the insertion of a rubber stopper.

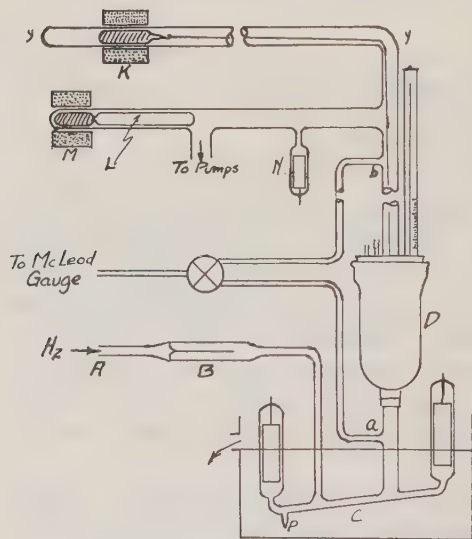


Fig. 1.

tions shown in the sketch. D is a calorimeter (shown in detail in Fig. 2) which could be slid up or down the tube ab. The calorimeter was made in the shape of a small Dewar flask with a hole in the bottom, the joint between the calorimeter and the central tube ab being made water tight by means of a short piece of gum tubing, E. The calorimeter was flared slightly at the top to permit the insertion of a rubber stopper.

² R. W. Wood, *Proc. Roy. Soc. London*, **97A**, 455 (1920); **102A**, 1 (1925); *Phil. Mag.*, **42**, 729 (1921); **44**, 538 (1922); Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924).

carrying a stirrer, F, a Beckmann thermometer, G, and a platinum heating unit, H, used to determine the heat capacity of the calorimeter. J was the catalytic surface causing the recombination of the atoms of hydrogen. It consisted of a cylinder of platinum foil fitting snugly inside the central tube and suspended from a fine nickel wire. The other end of this wire was fastened to a glass tube containing soft iron which could be moved along the tube by means of the electromagnet K (Fig. 1). In this way the platinum could be moved along the central tube with the calorimeter. The pressure in the apparatus was regulated by sliding the core L into or out of the gas stream by means of the electromagnet M. N is an auxiliary electrode whose use will be described below.

The tube ab was approximately one meter long and 0.8 cm. in internal diameter. The discharge tube was made of thin-walled 0.6-cm. tubing to facilitate cooling, the distance between the inlet and outlet taps being about 10 cm. The distance between the discharge and tap a was 8 cm. The electrodes were the usual cylinders of aluminum foil fastened to tungsten wires which were sealed through the pyrex. Rapid streams of water played over the exposed ends of the electrodes, thus preventing the conduction of heat from the discharge to the calorimeter. The volume of the calorimeter was slightly greater than 100 cc. The calorimeter stirrer was rotated by a small electric fan motor.

Procedure.—The primary consideration for experiments with atomic hydrogen is that the regions where it is to be produced and studied must be absolutely free from substances which may catalyze the recombination. Apparently all metals are active catalysts, together with porous or adsorbent surfaces. With this in mind the apparatus was designed to permit washing *in situ*. Each apparatus was made from new pyrex glass. After complete assembly aqua regia was forced through the arm P up to the top of the tube ab and then allowed to drain back. Of course, during the washing the platinum catalyst J was lifted out of range of the acid. The apparatus was then rinsed repeatedly with distilled water, after which the arm P was sealed off and the pump started. Before making any runs a discharge was passed from the auxiliary electrode N to the discharge tube. Bonhoeffer² has previously shown that this is useful in preparing a catalytically inert tube.

The foregoing procedure has been found in practically every instance to give apparatus in which reproducible results can be obtained. Presumably the aqua regia removes any metallic dust from the tube wall, the water fills up the pores in the wall and the discharge melts into the glass any active spots not removed by the acid. The discharge tubes show a pronounced fatigue effect after twenty to thirty hours of running. This fatigue is gradual and coincident with the appearance of appreciable quantities of sputtered material from the electrode. No successful method has so far been found for rejuvenating a spent tube.

The actual measurements were carried out as follows. The calorimeter and catalyst were set at the desired distance from the discharge and the pressure was allowed to reach the desired value; 100 cc. of distilled water, one or two degrees below room tem-

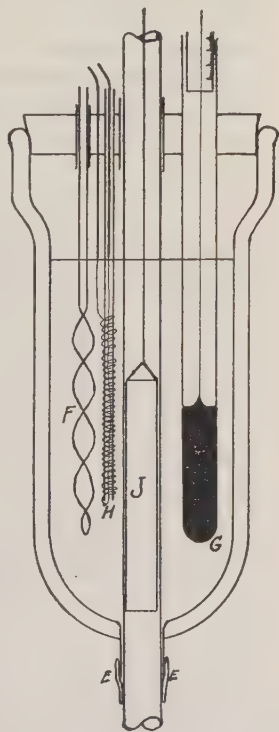


Fig. 2.

perature, was pipetted into the calorimeter and the stirrer started. After the warming of the calorimeter had reached a steady rate the Beckmann thermometer was read at one-minute intervals (timed by an electric clock) for a period of five minutes, in order to obtain the rate of warming at the start of the run. At the end of this period the discharge was turned on and the temperature readings were continued until the temperature rise was great enough to ensure the desired accuracy. This required ten minutes or less. The temperature measurements were continued for five minutes after the discharge was turned off to determine the final cooling curve. Fig. 3 shows several typical temperature-time curves. The pressure in the apparatus was measured at points a and b twice each during each run. The room temperature was maintained constant within 0.5° throughout each run.

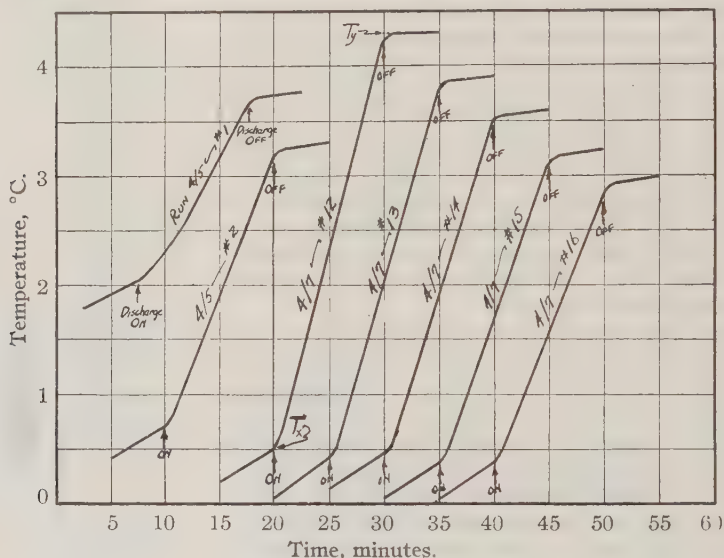


Fig. 3.

The heat capacity of the calorimeter was determined by noting the temperature rise caused by passing a current through the heating unit, H, the power input being measured by means of a milliammeter and millivoltmeter. The rate of flow of hydrogen was measured by disconnecting the hydrogen generator and allowing the hydrogen to be drawn instead from a gas buret.

Results

A series of preliminary experiments showed the qualitative conditions that must be fulfilled for the best production of atomic hydrogen. Aside from the necessity of the absence of catalysts, all the other variables affect the degree of dissociation of the hydrogen at a point some distance from the discharge. Thus the degree of dissociation is increased by high current density in the discharge and by water cooling the discharge. These two factors are, however, of secondary importance compared to the pressure and the quantity of hydrogen flowing. If the pumping capacity is approximately constant, these last two quantities are roughly proportional,

the pressure increasing if the quantity of hydrogen admitted to the apparatus is increased. Since the degree of dissociation at a point removed from the discharge decreases rapidly as the pressure increases, there will be some set of conditions for each apparatus at which the greatest amount of atomic hydrogen is obtained at a point outside the discharge. The pressure and the rate of flow at which the greatest amount of atomic hydrogen is obtained are determined by the efficiency of the pumps and the dimensions of the apparatus.

The best series of measurements of the rate of recombination are summarized in Table I and plotted in Fig. 4. The degree of dissociation is expressed by α , the fraction of the total amount of hydrogen which is present in the atomic form x cm. from the point of measurement of the initial pressure (P_0).

TABLE I
RESULTS OF MEASUREMENTS

Rate of flow of $H_2 = n_0 = 1.03 \times 10^{-5}$ moles/second. Primary current to transformer = 25 amps. Internal diameter of tube ab = 0.848 cm. Length ab = 108.3 cm. Heat capacity of calorimeter = $C = 121.5$ Cal./deg.

Date	No.	Dist. from a to calorim. x (cm.)	Press. (mm. Hg) meas. at		Temp. rise in calorim. °C.		Disso- ciation, 100 α , %
			a, P_0	b, P_1	$T_{obs.}$	$T_{corr.}$	
4/5	1*	86.2	0.524	0.150	2.53	1.62	31.6
	2*	86.2	.514	.142	2.51	2.14	41.8
	3	86.2	.584	.290	2.23	1.79	35.0
	4	86.2	.632	.356	2.04	1.48	29.0
	5	86.2	.714	.494	1.75	1.03	20.2
	6	86.2	.798	.584	1.23	0.77	15.1
	7	86.2	.508	.138	3.10	2.43	47.5
	8	65.9	.508	.140	3.43	2.73	53.4
	9	65.9	.642	.360	2.66	1.94	38.0
	10	65.9	.716	.484	2.36	1.44	28.2
	11	65.9	.788	.583	2.00	1.11	21.7
	12	65.9	.874	.684	1.44	0.87	17.0
	13	65.9	.508	.142	3.48	2.69	52.7
4/7	1*	65.9	.498	.134	3.27	2.57	50.3
	2	47.6	.488	.132	3.59	2.94	57.5
	3	47.6	.622	.360	2.98	2.25	44.0
	4	47.6	.696	.468	2.59	1.83	35.8
	5	47.6	.766	.568	2.33	1.45	28.4
	6	47.6	.850	.666	2.11	1.16	22.7
	7	31.6	.476	.136	3.25	3.23	63.2
	8	31.6	.616	.366	3.35	2.53	49.5
	9	31.6	.688	.474	2.73	2.25	44.0
	10	31.6	.762	.568	2.49	1.93	37.8
	11	31.6	.874	.666	2.08	1.53	29.9
	12	18.8	.488	.132	3.77	3.43	67.1
	13	18.8	.622	.364	3.43	3.01	58.9
	14	18.8	.694	.474	3.10	2.74	53.6
	15	18.8	.780	.570	2.79	2.39	46.8
	16	18.8	.834	.672	2.13	2.08	40.7

TABLE I (Concluded)

Date	No.	Dist. from a to calorim. x (cm.)	Press. (mm. Hg) meas. at		Temp. rise in calorim. °C.		Disso- ciation, 100 α , %
			a, P_0	b, P_1	$T_{\text{obs.}}$	$T_{\text{corr.}}$	
4/10	1	18.8	.502	.148	3.62	3.52	68.8
	2	8.3	.504	.148	3.93	3.89	76.1
	3	8.3	.642	.374	3.56	3.62	70.8
	4*	8.3	.708	.500	2.58	2.50	49.1
	5	8.3	.784	.578	3.06	2.96	57.9
	6	8.3	.864	.678	2.99	2.86	56.0
	7	8.3	.710	.490	3.35	3.38	66.2
	8	1.4	.496	.142	3.71	4.10	80.2
	9	1.4	.638	.394	3.39	3.91	76.5
	10	1.4	.710	.490	3.51	3.76	73.6

The pressures recorded are each the average of two readings taken during the particular run. During each of the runs the discharge was on for ten minutes except Run 4/7 No. 7, the time of which was eight minutes. The temperature-time readings were plotted on a large scale as soon as obtained.

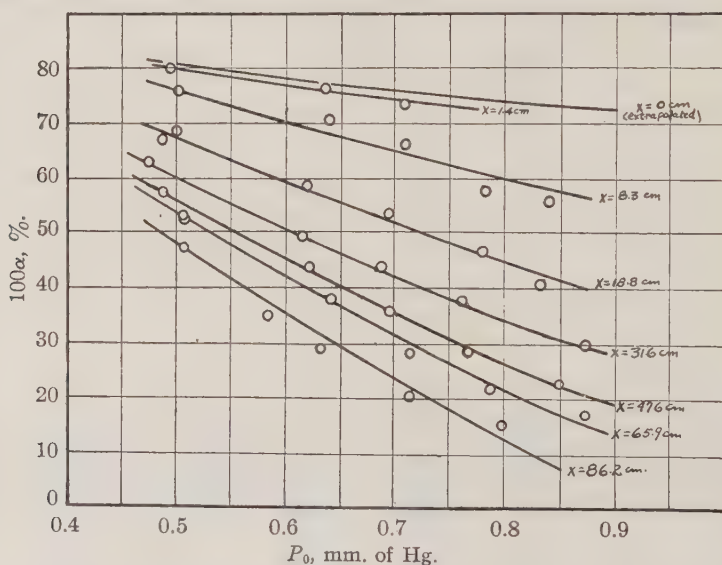


Fig. 4.

The observed temperature rise was obtained by subtracting the temperature at the start of the period when the discharge was on from the temperature obtained by extrapolation of the final cooling curve back to the time at which the discharge was turned off ($T_{\text{obs.}} = T_y - T_x$, Fig. 3). The correction for radiation and conduction of heat to or from the surroundings and for the heat of stirring was obtained by averaging the rate of cooling at the start and at the end, multiplying this average rate by the time during which the discharge was on and adding or subtracting, as the case

might be, to the observed temperature rise. The figures so obtained are tabulated under the heading " $T_{\text{corr.}}$ "

The fraction dissociated was calculated from the relation

$$\alpha = \frac{CT_{\text{corr.}}}{60 n_0 l \Delta H} \quad (1)$$

where ΔH is the heat of formation of one mole of molecular hydrogen from the atoms. This quantity was taken to be 100,400 Cal., which is an average of the values reported by Dieke and Hopfield,³ and Witmer⁴ from studies of the molecular spectrum of hydrogen. The " t " of Equation 1 stands for the time in minutes during which the discharge was on. The other symbols have the meanings assigned in Table I.

It will be noticed that the starred (*) runs of Table I are omitted from the plot of Fig. 4, since it was apparent from the varying slopes of the respective temperature-time curves that conditions changed during these runs. This discrepancy is of common occurrence and is undoubtedly due to a temporary catalytic effect. For example, if the apparatus is filled with air and left overnight, it requires from fifteen to twenty minutes' running before the degree of dissociation of the hydrogen outside the discharge builds up to a reproducible value, possibly due to a slow clean-up of oxygen adsorbed on the glass. This effect accounts for the first three inconsistent runs of Table I. It is readily recognized on the temperature-time curve, as may be seen by comparing the first two curves of Fig. 3. It is not evident in the first experiment of the third day since the discharge was run for thirty minutes before the runs were started. The other inconsistent run may have been caused by a catalytic particle working into the discharge and then being rendered inactive. It must be emphasized that, once active catalysts have been removed, the results do not depend on the apparatus. Duplicate runs which checked well within the experimental error have been made in different apparatus and at intervals of several weeks.

As will be pointed out below, an interpretation of the results requires a knowledge of the manner in which the pressure varied along the tube ab. An attempt was made to measure this, at the conclusion of the experiments, by sealing a number of taps into the tube and connecting these taps through stopcocks to the McLeod gage. The results so obtained are shown in Fig. 5, the dotted portions of the curves corresponding to the pressure drop caused by the presence of the platinum foil. Unfortunately some catalytic substance must have been present during these runs because the curves corresponding to the dissociated gas have the same slope as those for the molecular hydrogen. This would mean that the mixture of atomic and molecular hydrogen has the same viscosity as pure molecular

³ Dieke and Hopfield, *Z. Physik*, **40**, 299 (1926).

⁴ Witmer, *Phys. Rev.*, **28**, 1223 (1926).

hydrogen. That this is not the case has been shown by Harteck.⁵ It is much more probable that very little atomic hydrogen reached the Tube ab due to the presence of an active catalyst. There was no way of checking this point since the calorimeter was necessarily removed during the remodeling of the apparatus.

It was hoped at first that the method could be used to measure the rates of the gaseous reactions of atomic hydrogen. This could not be done, however, because these reactions take place along such a short interval of the tube (5–20 cm.) that accurate results could not be expected. In the

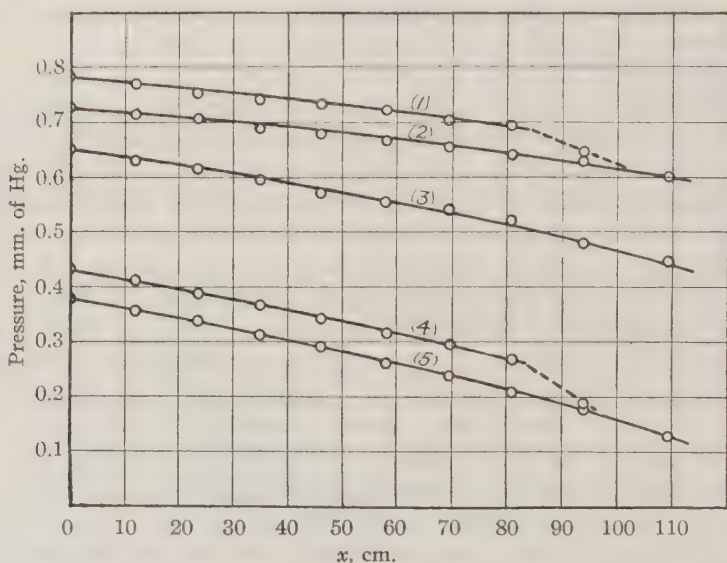


Fig. 5.—Curves 2, 3 and 5 obtained with discharge off and platinum out of outlet tube. Curves 1 and 4 obtained with discharge on and platinum at $x = 83$ cm.

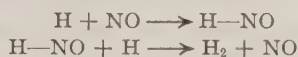
course of the preliminary experiments it was found, however, that if atomic hydrogen is led along a tube lined with a thin coating of sulfur, from $\frac{1}{6}$ to $\frac{1}{6}$ of the atomic hydrogen reacts to form hydrogen sulfide. This is to be expected since the first hydrogen sulfide formed rapidly catalyzes the recombination of the remainder of the hydrogen atoms.⁶

It was also found that nitric oxide catalyzes the recombination without itself being reduced. Analysis of the gases leaving the mixing chamber showed that over 99% of the nitric oxide was unchanged. However, a very minute amount of ammonia was formed in each case. Thus in one experiment 2.8×10^{-5} mole of ammonia was found while there were available 0.01 mole of atomic hydrogen and 0.0088 mole of nitric oxide.

⁵ P. Harteck, *Z. physik. Chem.*, **139A**, 98 (1928).

⁶ Boehm and Bonhoeffer, *ibid.*, **119**, 385 (1926).

This ammonia may have been due to the presence of nitrogen oxide as an impurity in the nitric oxide. Blank experiments showed that it was not present in the original hydrogen or nitric oxide and that it did not come from the combination in the discharge of the hydrogen with a small contamination of nitrogen. It is difficult to explain the catalysis of nitric oxide by means of a chain mechanism such as has been used by Bonhoeffer for the similar effect of hydrogen sulfide, hydrochloric acid, etc., since if the nitric oxide molecule is ever broken up it is extremely unlikely to form again under the conditions of the experiment. Possibly an unstable molecule of the type $\text{H}-\text{NO}$ is formed, in which case the mechanism would be



The $\text{H}-\text{NO}$ molecule might be quite short-lived and yet account for the effect.

The errors incident to this method of determining atomic hydrogen may be classified under four headings. In the first place the method is liable to the usual errors of calorimetry. These probably predominate in the present experiments, limiting the accuracy to 2-3%. Second, the method depends upon a knowledge of the heat of recombination of atomic hydrogen. This quantity, however, is now known with an accuracy within the above limits. Third, the heat effect registered in the calorimeter may be too small either because the recombination is not completely catalyzed by the platinum or because some of the heat is conducted away by the hydrogen stream. The first effect is extremely improbable since the rate of diffusion of atomic hydrogen under the conditions of the experiment is so high that a minute speck of metal in front of the calorimeter completely stops the heat effect. Further, in some of the preliminary experiments a thermometer with a silvered bulb was hung in the gas leaving the calorimeter and showed no temperature rise. Since the quantity of hydrogen flowing was small it would have had to be heated to an unreasonably high temperature to remove an appreciable amount of heat from the system. Finally, heat may be brought to the calorimeter in other ways than by the recombination of the atoms. Thus heat may be conducted from the discharge along the glass walls. This, however, was too small to affect the results since, when the whole discharge tube was water cooled, numerous runs in catalytically active apparatus showed no heat effect. This fact also removes the possibility of metastable molecules bringing energy to the calorimeter. It might also be supposed that, since the atomic hydrogen is recombining along the tube between the calorimeter and the discharge tube, sufficient heat could be liberated to affect the results. This is unlikely since in some of the preliminary experiments this tube was water cooled without affecting the results.

The accuracy of the method, therefore, is limited by the errors involved in the calorimetry of quantities of heat which, in this case, varied from 5 to 40 Cal. per minute.

The Three-Body Mechanism

It will now be shown that the results summarized in Table I are in accord with the predicted mechanism of recombination by triple impacts. The fundamental assumption is that at constant pressure

$$-\frac{dN_H}{dt} = 2\Sigma\nu_3 \quad (2)$$

where N_H is the number of hydrogen atoms per cc. at the time t and $\Sigma\nu_3$ is the number of triple impacts per second per cc. in which at least two of the colliding bodies are hydrogen atoms.

There is considerable uncertainty as to the quantitative definition of a three-body collision. Whatever be the definition, however, $\Sigma\nu_3$ may be set equal to

$$\Sigma\nu_3 = K_1 N_H^2 + K_2 N_H^3 + K_3 N_H^2 N_{H_2} \quad (3)$$

where K_1 , K_2 and K_3 are proportionality constants and N_{H_2} is the number of hydrogen molecules per cc. The first term on the right of Equation 3 takes account of triple impacts in which the wall is the third body. In the second term the third body is a hydrogen atom and in the third a hydrogen molecule.

To express the present results it will be necessary to take account of the fact that the atomic hydrogen is recombining at variable pressure while flowing along the tube. This may be accomplished by writing the equation of continuity of the hydrogen atoms

$$\frac{\partial N_H}{\partial t} - \frac{\partial(N_H u)}{\partial x} = 0 \quad (4)$$

where u is the linear velocity of the gas at the point x

$$u = \frac{n}{\pi r^2 \left(N_{H_2} + \frac{1}{2} N_H \right)} \quad (5)$$

Here n is the number of hydrogen molecules admitted to the apparatus per second ($n = n_0 N_A$). Since

$$N_H + N_{H_2} = \frac{P}{kT} \quad (6)$$

and

$$\alpha = \frac{N_H}{2N_{H_2} + N_H} \quad (7)$$

$$N_H = \frac{P}{kT} \times \frac{2\alpha}{1 + \alpha} \quad (8)$$

$$N_{H_2} = \frac{P}{kT} \times \frac{1 - \alpha}{1 + \alpha} \quad (9)$$

Substituting Equations 2, 3, 5, 8 and 9 in Equation 4, there is obtained

$$\frac{-\partial\alpha}{\partial x} = \frac{\pi r^2}{n} \times K_1 \frac{4\alpha^2 P^2}{(1+\alpha)^2 k^2 T^2} + K_2 \frac{8\alpha^3 P^3}{(1+\alpha)^3 k^3 T^3} + K_3 \frac{4\alpha^2(1-\alpha)P^3}{(1+\alpha)^3 k^3 T^3} \quad (10)$$

Equation 10 cannot be integrated except by means of a series development. It is possible, however, that any one of the three terms may predominate. To integrate these three simplified equations it will be necessary to know P as a function of x . This pressure gradient could be calculated from the data of Harteck⁵ but this would make the computations quite complicated. Since Harteck found that the viscosity of mixtures of atomic and molecular hydrogen does not differ greatly from the value for molecular hydrogen alone, it is believed that an empirical method will be sufficiently accurate for the present purposes. It will therefore be assumed that

$$P = \sqrt{P_0^2 - \beta x} \quad (11)$$

where β is a constant to be evaluated from the data of each experiment. This equation is equivalent to the assumption that the viscosity of the gas is constant along the tube. In order to calculate the constant β it may reasonably be assumed that, since all of the hydrogen is molecular after leaving the calorimeter, the curves of Fig. 5 give the true pressure gradient for this part of the flow. If this is the case it is possible to determine the pressure P at the calorimeter from the measured value of P_1 , by interpolation. Since P , P_0 and x are known, β may be calculated for each run. Although this method of calculation is approximate, the results seem fairly certain for large values of x . Thus in the first five of the runs calculated in Table II β varies irregularly between 3520 and 4440 (pressure expressed in dynes/cm.²). In the last five runs β decreases fairly regularly from 4160 to 3190. The calculated value of β for molecular hydrogen is 3570.

Using the assumption of Equation 11 and setting alternately K_2 and K_3 , K_1 and K_3 , K_1 and K_2 equal to zero, the following equations are obtained

$$K_1 = \frac{nk^2T^2 \left[\frac{1}{\alpha} - \frac{1}{\alpha_0} + 2 \ln \frac{\alpha_0}{\alpha} + \alpha_0 - \alpha \right]}{4\pi r^2 \left(P_0^2 x - \frac{\beta x^2}{2} \right)} \quad (12)$$

$$K_2 = \frac{5\beta nk^3T^3 \left[\frac{1}{2} \left(\frac{1}{\alpha^2} - \frac{1}{\alpha_0^2} \right) + 3 \left(\frac{1}{\alpha} - \frac{1}{\alpha_0} \right) + 3 \ln \frac{\alpha_0}{\alpha} + \alpha_0 - \alpha \right]}{16\pi r^2 [P_0^5 - (P_0^2 - \beta x)^{5/2}]} \quad (13)$$

$$K_3 = \frac{5\beta nk^3T^3 \left[4 \ln \frac{\alpha_0}{\alpha} + 8 \ln \frac{1-\alpha}{1-\alpha_0} + \frac{1}{\alpha} - \frac{1}{\alpha_0} - (\alpha_0 - \alpha) \right]}{8\pi r^2 [P_0^5 - (P_0^2 - \beta x)^{5/2}]} \quad (14)$$

Equation 12 embodies the assumption that the recombination of hydrogen atoms is largely heterogeneous; Equation 13 that it is homogeneous;

ous, but that only the hydrogen atoms can act as the third body; and the last equation that only the hydrogen molecule can act as the third body. Table II summarizes the values of these constants calculated from some of the experiments of Table I. The values of α_0 used in the calculations were taken from the extrapolated curve of Fig. 4.

TABLE II
SUMMARIZED VALUES OF CONSTANTS

P_0	x	α_0	α	$K_1 \times 10^{15}$	$K_2 \times 10^{32}$	$K_3 \times 10^{32}$
0.508	86.2	0.810	0.475	4.20	4.20	12.40
.584	86.2	.790	.350	4.24	3.60	9.04
.632	86.2	.778	.290	4.68	4.16	8.24
.714	86.2	.758	.202	5.04	4.72	6.32
.798	86.2	.740	.151	5.20	4.96	4.84
.508	65.9	.810	.534	3.84	3.48	14.44
.642	65.9	.775	.380	3.76	2.84	7.44
.716	65.9	.758	.282	4.24	3.24	6.04
.788	65.9	.743	.217	4.44	3.48	4.88
.874	65.9	.728	.170	5.12	3.60	3.88

Each of the three constants shows a well-defined drift so that it may be concluded that none of the three equations expresses the actual mechanism of recombination. The variation of the constants, however, is such as to make it seem probable that the differential Equation 10 does express the correct mechanism. Thus as the pressure is increased the apparent value of K_1 increases, K_2 first decreases and then increases and K_3 decreases. The increase in K_1 indicates that there is relatively less recombination taking place on the wall at the high pressures. Similarly, the decrease of K_3 shows that there are relatively more effective collisions involving two hydrogen atoms and one hydrogen molecule at the higher pressures. These two effects combined can account for the changes in K_2 . Thus increasing the pressure lessens the relative amount of wall reaction, which would cause K_2 to decrease, and increases the relative amount of recombination caused by the molecules, which would cause K_2 to increase. Since the wall reaction varies as the square of the pressure and the "molecule reaction" as the pressure cubed, the first effect predominates at the low pressures and the second at the higher pressures. K_2 , therefore, passes through a minimum.

An attempt was made to calculate the constants directly from the differential equation, by obtaining the slope graphically. This is a very unfavorable way of calculating the data since the determinants of the various sets of equations nearly vanish. Thus a change of 2% in the slope changes the constants by a factor of 100 or more.

A series of approximate calculations, however, indicated that the data would be satisfied if K_1 , K_2 and K_3 are of the orders of magnitude 10^{-16} , 10^{-32} and 10^{-32} , respectively.

The approximate values of the constants so obtained may render possible a more quantitative definition of a three-body collision. Thus a three-body collision in which the wall is the third body may be defined as a collision between two hydrogen atoms occurring less than a short distance, δ , from the wall. In other words, the number of such collisions per second per cc. equals the number of collisions between hydrogen atoms per sec. per cc. times the volume of a cylindrical shell of radius r , thickness δ and length such that the volume inclosed by the shell shall be 1 cc. That is

$$\nu_{s(\text{wall})} = 2N_{\text{H}}^2\sigma_{\text{H}}^2\sqrt{\frac{\pi kT}{m_{\text{H}}}} \times \frac{2\delta}{r} \quad (15)$$

where σ_{H} is the diameter and m_{H} the mass of the hydrogen atom. Therefore

$$K_1 = \frac{4\sigma_{\text{H}}^2\delta}{r}\sqrt{\frac{\pi kT}{m_{\text{H}}}} \quad (16)$$

In arriving at this relation it is assumed that the tube wall is perfectly smooth. Although this cannot be the case, the actual area of the wall is probably not greatly different from the assumed value since the small adsorbing pores of the wall are filled with water. Substitution of numerical values in Equation 16 shows that δ is of the order of magnitude of 10^{-7} cm. Irregularities in the wall would decrease this figure. In the calculation the diameter of the hydrogen atom has been assumed to be 2×10^{-8} cm.

A three-body collision involving three molecules may be defined in a number of different ways. For example, Tolman⁷ defines it as one in which the distances between Molecule I and Molecule II and between Molecule II and Molecule III are equal to or less than some short distance, δ . From the relation obtained by him it follows that

$$K_2 = 32\pi^2\sigma_{\text{H}}^4\delta\sqrt{\frac{kT}{\pi m_{\text{H}}}} \quad (17)$$

and

$$K_3 = 16\pi^2\sigma_{\text{H}}^2\left(\frac{\sigma_{\text{H}} + \sigma_{\text{H}_2}}{2}\right)^2\delta\sqrt{\frac{kT}{\pi m_{\text{H}}}}\left(1 + \sqrt{\frac{m_{\text{H}} + m_{\text{H}_2}}{m_{\text{H}_2}}}\right) \quad (18)$$

where σ_{H_2} and m_{H_2} are, respectively, the diameter and mass of the hydrogen molecule. From either equation it is found that δ is of the order of magnitude 10^{-9} cm.

The definition suggested by Herzfeld¹ and used by Bodenstein⁸ in his calculations of the rate of the reaction between NO and O₂ is identical with the above except that δ is identified as the diameter of the colliding molecules. The expressions obtained from the two definitions for the number of triple collisions differ only by a numerical factor of the order ten.

⁷ Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," The Chemical Catalog Co., New York, 1927, p. 247.

⁸ Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

Syrkin⁹ has calculated the number of multiple collisions between point molecules by defining a multiple collision as one in which the colliding molecules are within a small sphere of radius r . Applying his general equation to the present case, there are obtained the equations

$$K_2 = \frac{\left(\frac{4}{3}\pi r^3\right)^2}{3!r} \times \frac{2}{3} \sqrt{\frac{2\pi kT}{m_H}} \quad (19)$$

$$K_3 = \frac{\left(\frac{4}{3}\pi r^3\right)^2}{2!r} \times \frac{2}{3} \sqrt{2\pi kT} \sqrt{\frac{2}{m_H} + \frac{1}{m_{H_2}}} \quad (20)$$

From either equation r is found to be of the order 10^{-8} cm.

It may therefore be concluded that the recombination of hydrogen atoms proceeds according to the predicted three-body mechanism. The experimental proof, however, is not as definite as might be desired since no integral of Equation 10 was obtained. For this reason the experimental method was not considered suitable for an investigation of the effect of mixing other gases with the dissociated hydrogen.

There are a number of other possible mechanisms for the recombination of atomic hydrogen. Thus it might be supposed that even under the best circumstances the walls of the containing vessel still exert a specific catalytic power at relatively isolated points. If, however, this were the principal means of recombination, K_1 calculated from Equation 12 should be constant. It might further be supposed that the water vapor present in the gas might enter into the mechanism. The fact that Bonhoeffer¹⁰ and Mohler¹¹ have shown that the OH bands are excited by atomic hydrogen might be cited as evidence in favor of this statement. Since, however, the reaction



is endothermic, it may be ruled out. It seems more probable that unexcited OH molecules are produced in the discharge tube and that the bands result from triple impacts between these and two hydrogen atoms. Under the conditions of the present measurements such an effect would be too small to influence the results.

No account has been taken of the possibility of recombination taking place in the adsorbed phase. Langmuir¹² has shown that atomic hydrogen is appreciably adsorbed by glass surfaces at room temperature but in his experiments the glass was thoroughly baked out prior to the adsorption while in the present case the tube wall was covered with a film of water. Furthermore, if the wall were covered with a reactive adsorbed film the

⁹ Syrkin, *Physik. Z.*, **24**, 236 (1923).

¹⁰ Bonhoeffer, *Z. physik. Chem.*, **116**, 391 (1925).

¹¹ Mohler, *Phys. Rev.*, **29**, 419 (1927).

¹² I. Langmuir, *THIS JOURNAL*, **34**, 1310 (1912); **36**, 1711 (1914); **37**, 417 (1915); **38**, 2270 (1916).

recombination would be at least 10^5 times more rapid. In the light of these facts it seems extremely improbable that the wall as a whole adsorbs atomic hydrogen. There remains the possibility that isolated points on the wall are absorbent and hence catalytic. Such a possibility is unlikely since if this were the case duplicate results could not be obtained in different apparatus.

In conclusion the author wishes to express his indebtedness to Dr. H. C. Urey and to Professor K. F. Herzfeld for their advice during the course of this work.

Summary

1. A calorimetric method for the estimation of the amount of atomic hydrogen obtained from a Wood tube is described, together with the application of this method to the measurement of the rate of recombination of the hydrogen atoms.

2. This rate has been measured through the pressure range 0.5–0.9 mm. of mercury.

3. It was found that, under the conditions of the experiment, one-fifth to one-sixth of the atomic hydrogen present reacted with solid sulfur and that nitric oxide catalyzes the recombination of the atomic hydrogen.

4. The data obtained for the rate of recombination are discussed and it is concluded that they are in accordance with the predicted three-body mechanism.

BALTIMORE, MARYLAND

BIOGRAPHY

Hugh Molleson Smallwood, son of Julian Chase Smallwood and Madeline Church (Foster) Smallwood, was born at Perth Amboy, N. J. October 25, 1903. He received his preliminary education in the Public Schools of Syracuse, N. Y. and in the Friends High School, Baltimore, Md. and was graduated from that Institution in June 1920. He entered the Department of Engineering in The Johns Hopkins University in September of the same year, receiving the degree of Bachelor of Science in Chemistry June 1924. Since September 1924 he has been engaged in graduate work in Chemistry in the Johns Hopkins.

During the year 1925-26 he was Student Assistant in Chemistry and during the year 1926-27 he was holder of a DuPont Fellowship. He completed his work in June 1927.

